

SUBSTITUTED 1-PHOSPHABICYCLO[3.2.0]HEPT-4-ENES

Ju.G.Trishin<sup>b</sup>, I.V.Konovalova<sup>a</sup>, R.N.Burangulova<sup>b</sup>,  
L.A.Burnaeva<sup>a</sup>, V.N.Chistokletov<sup>b</sup>, A.N.Pudovik<sup>a</sup>

<sup>a</sup> V.I.Ul'yanov-Lenin Kazan State University, Department of  
Chemistry, Kazan, 420008, USSR

<sup>b</sup> Leningrad Technology Institute for the Pulp and Paper  
Industry, Leningrad, 193092, USSR

**Abstract.** The interaction between dialkyl alkynylphosphonites and pyruvic acid methyl ester in boiling benzene afforded 1,1-dialkoxy-3,6-dimethyl-3,6-di(methoxycarbonyl)-4R-2,7-dioxa-1-phosphabicyclo[3.2.0]hept-4-enes.

Trialkyl phosphites and dialkyl phosphonites react with pyruvic acid esters to form 1,3,2-dioxaphospholanes at 0 ÷ -10°C and at 100°C the mixtures of 1:1 and 1:2 adducts of the open chain or dioxaphospholane structure respectively<sup>1,2</sup>. The interaction between dialkyl isocyanatophosphites, hetero- $\alpha,\beta$ -unsaturated P(III) compounds, and pyruvic acid esters leads to 1:1 heterocyclic adducts - substituted 1,4,3, $\lambda^5$ -oxazaphospholidines resulting from the involvement in the reaction both phosphorus atom and isocyanate multiple bond<sup>3</sup>.

The results obtained show, that in contrast to isocyanatophosphites, dialkyl phosphonites containing triple C $\equiv$ C bond react with pyruvic acid methyl ester to form 1:2 adducts - 1,1-dialkoxy-3,6-dimethyl-3,6-di(methoxycarbonyl)-4R-2,7-dioxa-1-phosphabicyclo[3.2.0]hept-4-enes (1-3). The latter are representatives of new type unsaturated heterocycles containing phosphorus.

The reaction are likely to start with the nucleophilic attack of a phosphorus atom to the carbon of a carbonyl group. The resulting bipolar ion (1a-3a) transforms into ion (1b-3b) in a manner of phosphonate-phosphate rearrangement. The carbanion of the bipolar ion (1b-3b) adds to  $\beta$ -carbon atom of the activated C $\equiv$ C bond to give cyclic ylide (1c-3c). Addition of the second molecule of pyruvic acid ester leads to ylide stabilization. In a similar manner the interaction of diphenylvinylphosphine with hexafluoroacetone is known to occur<sup>4</sup>.

The reactions of dialkyl alkynylphosphonites with pyruvic acid methyl ester were conducted under the reagent ratios both 1:1 and 1:2. In either